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UNITED STATES
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HAROLD L. ICKES, SECRETARY

BUREAU OF MINES
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BUREAU OF MINES HALDANE GAS-ANALYSIS APPARATUS

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BY

L. B. BERGER AND H. H. SCHRENK

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

BUREAU OF MINES HALDANE GAS-ANALYSIS APPARATUS[1]

By L. B. Berger[2] and H. H. Schrenk[3]

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INTRODUCTION

The Haldane gas-analysis apparatus used by the Bureau of Mines is patterned after the device developed by Haldane 4/ and differs from it only in structural modifications that have been added to facilitate operation and simplify construction.

The apparatus was developed to permit determination of carbon dioxide, combustible gases, and oxygen with a degree of accuracy not attainable with apparatus of the types ordinarily used for the analysis of fuel gases, flue gases, and similar mixtures. The Haldane apparatus is used by the Bureau of Mines chiefly in the analysis of air samples collected in coal and metal mines and other underground workings and is applied also in the analysis of many other types of gas mixtures when accurate determination of certain constituents is desired.

4/ Haldane, J. S., Some Improved Methods of Gas Analysis: Jour. Physiol., vol. 22, 1898, pp. 465-480; A Rapid Method of Estimating Carbon Dioxide in Air: Jour. Hygiene, vol. 1, 1901, pp. 109-114; Methods of Air Analysis: London, 1912. Revised and reprinted 1918. Reprinted 1920. Revised, in collaboration with J. Ivon Graham, and reprinted 1935. Foster, C. LeN. and Haldane, J. S., The Investigation of Mine Air: London, 1905, pp. 100-120.

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PURPOSE OF PUBLICATION

The purpose of this publication is to supplement information contained in an earlier Bureau of Mines bulletin[5] with a description of improvements in design and to add to the instructions in technique comments that may be helpful to users of the Haldane apparatus.

ACCURACY AND PRECISION OF THE HALDANE APPARATUS

The Haldane apparatus is of advantage chiefly in determining constituents of gas mixtures that are present in amounts too small for accurate determination by ordinary gas-analysis methods. The accuracy and precision of the Haldane method in the determination of carbon dioxide, a single combustible gas, and oxygen are 0.02 to 0.03 percent[6] compared to 0.10 to 0.20 percent, or more, in ordinary gas-analysis methods. When more than one combustible gas is present in the mixture the accuracy and precision of determination may be reduced, as is indicated later.

The accuracy and precision attainable with the Haldane apparatus are essential in many instances to obtain analytical results of value. Determination of methane in the ventilating air currents of coal mines illustrates this point. The methane content of the main-return air current may be used to calculate the quantity of methane liberated by a mine over a given period. If a main-return air current of 100,000 cubic feet per minute contains 0.10 percent methane, the mine is liberating 144,000 cubic feet of methane in 24 hours. Results of little or no value will be obtained if the methane content of this air is determined by methods having possible errors approximating the concentration of methane actually present.

LIMITATIONS OF THE HALDANE APPARATUS

The Haldane burette, in which gas volumes are measured is so constructed that the gas mixture undergoing analysis must contain approximately 75 percent of inert gas, such as nitrogen, or a similar percentage of a constituent that is not determined.

In determining combustible gases, the Haldane apparatus is limited to mixtures that do not contain combustibles in sufficient quantity to be inflammable (see Appendix) and that contain enough oxygen to burn completely all combustible gas present. Gas samples containing combustibles in amounts within or above the inflammable limits must be analyzed by other means.

5/ Burrell, G. A., and Seibert, F. M., Sampling and Examination of Mine Gases and Natural Gas: Bull. 197, Bureau of Mines (revised in 1926 by G. W. Jones), 103 pp.

6/ This does not mean that the accuracy is 0.02 to 0.03 percent of the amount of a constituent found by analysis, but that the results as expressed in percent do not deviate more than 0.02 to 0.03 from the amount of that constituent actually present. In terms of precision it means that duplicate analyses agreeing within 0.02 to 0.03 when expressed in percent are attainable.

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The Haldane apparatus is restricted, therefore, to certain types of gas mixtures, and because of its accuracy and precision is of special value in their analysis.

PRINCIPLES OF GAS-VOLUMETRIC ANALYSIS AS APPLIED IN THE HALDANE APPARATUS

The analysis of a gas mixture by the gas-volumetric method involves subjecting a measured volume of the mixture to successive treatments, each of which effects removal of a specific constituent of the mixture. Measurement of the decreased volume caused by each such removal permits calculation of the relative proportions of the various constituents in the mixture.

In determining carbon dioxide, combustible gases, and oxygen with the Haldane apparatus this procedure is applied by measuring the gas volumes in a burette, which is essentially a graduated glass tube. Carbon dioxide is removed by passing the gas from the burette into a pipette that contains an alkaline medium, such as potassium hydroxide solution. Combustible gases are determined by passing the gas sample into a pipette containing an electrically heated platinum wire that causes these gases to burn. Carbon dioxide produced by combustion is removed by again passing the gas into the potassium hydroxide solution. Osygen is determined by passing the gas into a pipette that contains an oxygen-absorbing medium, such as potassium pyrogallate solution. The gas sample is confined in the burette by a column of mercury, the level of which may be raised and lowered, thus forcing the gas alternately from the burette to the pipettes through suitable communicating tubes. Gas volumes measured in the burette are brought to comparable conditions of temperature and pressure by a compensating device attached to the burette.

FACTORS THAT AFFECT THE ACCURACY OF ANALYSIS

In gas-volumetric analysis certain factors must be considered if results of maximum accuracy are to be obtained. The most important of these, as related to analysis in the Haldane apparatus, are discussed in the following paragraphs.

Change of Temperature and Barometric Pressure During Analysis

As gas-volumetric analysis consists of a series of measurements of change of volume caused by removal of the various constituents of a mixture, all other factors tending to cause change of volume must be eliminated. The volume of a gas changes with temperature, provided the pressure remains constant, therefore considerable error might be introduced by variations in temperature during analysis unless correction is made for them by calculation, or they are compensated for by the design of the apparatus. Likewise correction or compensation must be made to avoid errors from changes in gas volume due to variations in barometric pressure during analysis.

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The Haldane apparatus is equipped with a device that compensates for changes in temperature or pressure, eliminating the necessity for correction of gas volumes to standard conditions by calculation. All gas volumes measured in the burette are balanced against a fixed volume of gas contained in a closed tube in a water-jacket that also surrounds the burette. Any temperature change that occurs in the apparatus during analysis affects the gas in the burette and in the closed compensator tube to the same extent, and the temperature effect is nullified or canceled. As the gas volumes measured in the burette are balanced against a fixed volume of gas in the compensator tube, compensation for changes in barometric pressure is also obtained. The use of the compensating device is described in the instructions for operating the apparatus.

Change of Water-Vapor Content of Gas Sample During Analysis

As a volume of gas may contain varying amounts of water vapor, depending upon temperature and degree of saturation of the gas with water vapor, this condition must be controlled in gas-analysis procedures to prevent changes in gas volume by the presence of varying amounts of water vapor during analysis.

In the Haldane apparatus the gas is kept completely saturated with water vapor by maintaining a small amount of water in the burette at all times. If this procedure were not followed, a sample of dry or incompletely saturated gas, passed into the potassium hydroxide solution for the determination of carbon dioxide, would gain water vapor from the solution, and the determination would be in error by the amount of water vapor gained. A small amount of water is also maintained in the closed compensator tube, and the effect of variation in water-vapor pressure caused by temperature changes is nullified, as the gas in both burette and compensator tube is affected to the same extent.

Solubility of Gases in Confining Liquids

All gases are soluble to some extent in water, and if water were used as the confining liquid considerable error would be introduced through solubility. To eliminate this source of error mercury is used as the confining liquid in the burette and combustion pipette and for displacing gas from the sample container into the burette.

Solubility of Gases in Reagents

In the use of reagents such as potassium hydroxide and potassium pyrogallate solutions physical solution of some of the constituents of the gas sample is possible, in addition to removal by chemical action of the constituent for which the reagent is specifically intended. Potassium hydroxide solution exerts no significant solvent action on gases, such as oxygen, nitrogen, methane, carbon monoxide, and hydrogen, that may come into contact with it during the determination of carbon dioxide, and after one or two analyses are made the solubility error becomes negligible. In the case of potassium pyrogallate solution, however, there is appreciable solubility of nitrogen until the reagent has become saturated with that gas. When a fresh solution of potassium

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pyrogallate is used in the apparatus at least two analyses should be made before the oxygen values obtained are taken as correct. When gases and vapors such as unsaturated hydrocarbons, gasoline, and benzol are determined in the Haldane apparatus, considerable solution of these compounds may occur if the sample is passed into the potassium hydroxide solution before combustion. In such instances a modified procedure, described later, usually will eliminate this error.

Calibration of the Burette

Burettes usually are graduated as accurately as possible, but it is difficult to obtain extreme accuracy over the entire length of a burette of the small diameter used in the Haldane apparatus. Consequently, it is advisable to calibrate the burette before use. The procedure for calibrating burettes is included under comments on use and care of apparatus.

DESCRIPTION OF APPARATUS

A diagrammatic sketch of the Haldane apparatus is shown in figure 1.

Burette

Burette f has a total capacity of 21 ml. The bulb at the upper part of the burette has a capacity of 15 ml and is not divided by graduations. The capacity of the stem below the bulb is 6 ml, graduated in hundredths of a milliliter. Graduation of the burette starts at the bottom of parallel-bore stopcock e. This stopcock may be turned to communicate through stopcock d and capillary glass tubing c to sample container a, or may be rotated from this position through 180° to communicate with pipettes l, m, and n through the capillary glass manifold and stopcocks i, j, and k. The burette is enclosed in a water jacket, g, to protect it from sudden temperature changes. A tube connected to a compressed air supply extends nearly to the bottom of the water jacket, and a stream of air bubbles escaping from this tube produces circulation and uniformity of temperature of the water in the jacket. The lower end of the burette is connected by heavy-walled rubber tubing to leveling bulb s, which rests in movable support t.

Pipettes

Pipette l is for the potassium hydroxide solution used in determinating carbon dioxide. The lower outlet of this pipette communicates through rubber tubing connections with reservoir r and capillary glass tube o''', which is part of the compensating device. Reservoir r is adjustable vertically.

Combustion pipette m contains a spiral of No. 26 or 28 B. & S. gage platinum wire, which may be heated electrically to cause burning of combustible gases. Mercury is used as the confining liquid in this pipette. Two glass tubes support the spiral and are filled with mercury to serve as conductors for the electric current. The upper ends of these tubes are open, and each tube has a short stud of No. 20 B. & S. gage

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platinum wire sealed to the glass in a vertical position at the opening. These studs furnish electrical contact between the mercury and the spiral, which is held in place by winding its ends around the studs. The lower ends of the tubes are sealed closed around two short lengths of No. 20 B. & S. gage platinum wire, to which are attached wires p and p' connecting to the electrical supply.

Pipette m is connected by rubber tubing to reservoir m', which is mounted on a slide movable vertically by a rack and pinion gear, w, attached to the reverse side of the apparatus. Reservoir m' is mounted in this manner so that it may be lowered and raised as gas is passed into and withdrawn from pipette m, keeping the mercury at approximately the same levels in m and m', thus maintaining the gas in m at approximately atmospheric pressure, thereby reducing the possibility of leakage owing to excessive pressures on the rubber tubing. The level of the mercury in reservoir m' may be observed through slot v in the board on which the apparatus is mounted.

Pipette n holds the potassium pyrogallate solution used in determination of oxygen. The lower outlet of this pipette is connected to reservoir n', the top outlet of which is connected to a rubber bag, u, that protects the reagent from the oxygen of the air.

Pipettes l and n contain a number of lengths of small-diameter shell tubing which, when gas is passed into the pipettes, presents a considerable surface wet with reagent, accelerating absorption of gas. The tubes are supported at their lower ends by a helix of glass rod perpendicular to the longitudinal axes of the tubes.

Compensator

Closed tube q of the compensating device is shown in water jacket g. The upper end of this tube is connected through capillary glass tubing to tube o'''. Stopcock h is used to bring the pressure in the closed tube to atmospheric before starting an analysis.

Connections to Gas Sample

The gas sample bottle, a, shown in mercury jar b is the vacuum type used by the Bureau of Mines in sampling mine atmospheres. A sealed sample bottle is shown at a'. With bottles of this type the gas sample is transferred to the burette by U-tube c. If other types of sample bottles are used, for example those having stopcocks at both ends, c may be replaced by a short elbow of capillary glass tubing.

Electrical Accessories

Electrical accessories used in conjunction with the combustion pipette are indicated in the wiring diagram shown in figure 1. A current supply at 6 to 8 volts is necessary. One side of the circuit starts from the source of current supply, passes through switch x and variable resistance y to lead p, connecting to one of the platinum stud terminals of the combustion pipette. The current passes through the platinum

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spiral to the other terminal and lead p', which returns to the source of supply. Variable resistance y may be a rheostat of the carbon pile type used for radio-tube filament control or a length of wire having a resistance of 1 to 2 ohms and equipped with a movable contact. Where alternating current is available a step-down transformer furnishing current at 6 to 8 volts may be used as the power supply. The capacity of the transformer should be at least 150 watts. Where only direct current is available a lamp bank or other suitable resistance may be used. Storage batteries or dry cells may be employed but are not particularly satisfactory, as storage batteries require frequent recharging, and dry cells are rapidly depleted.

PREPARATION OF SOLUTIONS

Potassium Hydroxide

The potassium hydroxide solution used for determining carbon dioxide is prepared by dissolving 300 grams of potassium hydroxide (electrolytic) in 1000 ml of water. Although potassium hydroxide is preferable, a solution of 200 grams of sodium hydroxide in 1,000 ml of water also can be used. There is greater tendency, however, toward the deposition of bicarbonate with sodium hydroxide than with potassium hydroxide.

Potassium Pyrogallate

The potassium pyrogallate solution used for determination of oxygen is prepared as follows: Dissolve 50 grams of pyrogallic acid in 150 ml of water and disolve 1,200 grams of potassium hydroxide (electrolytic) in 800 ml of water. When the potassium hydroxide solution has cooled, measure 250 ml of the solution into each of a number of bottles of approximately 325 ml capacity, such as magnesium citrate bottles. Add 45 ml of the pyrogallic acid solution to each bottle, close immediately, and mix. A number of small bottles are preferable to one large one, as only a small portion of the solution is exposed to the oxygen of the air when the bottle is opened, whereas if stored in a single large container all the solution would be exposed each time the container was opened.

PREPARATION OF APPARATUS FOR USE

Assembling Burette

Burette f (fig. 1) is filled by adding clean (preferably distilled) mercury through leveling bulb s with stopcock e open. Mercury is added until, with s raised so that the mercury rises to stopcock e, only a few ml of mercury remain in s.

Two or three ml of water are added to the compensator tube q before it is inserted in the water jacket. Tubes q and o''' are connected by rubber tubing as shown, and the water jacket is filled with water. Stopcock e is connected to the manifold and to stopcock d and U-tube c by rubber tubing.

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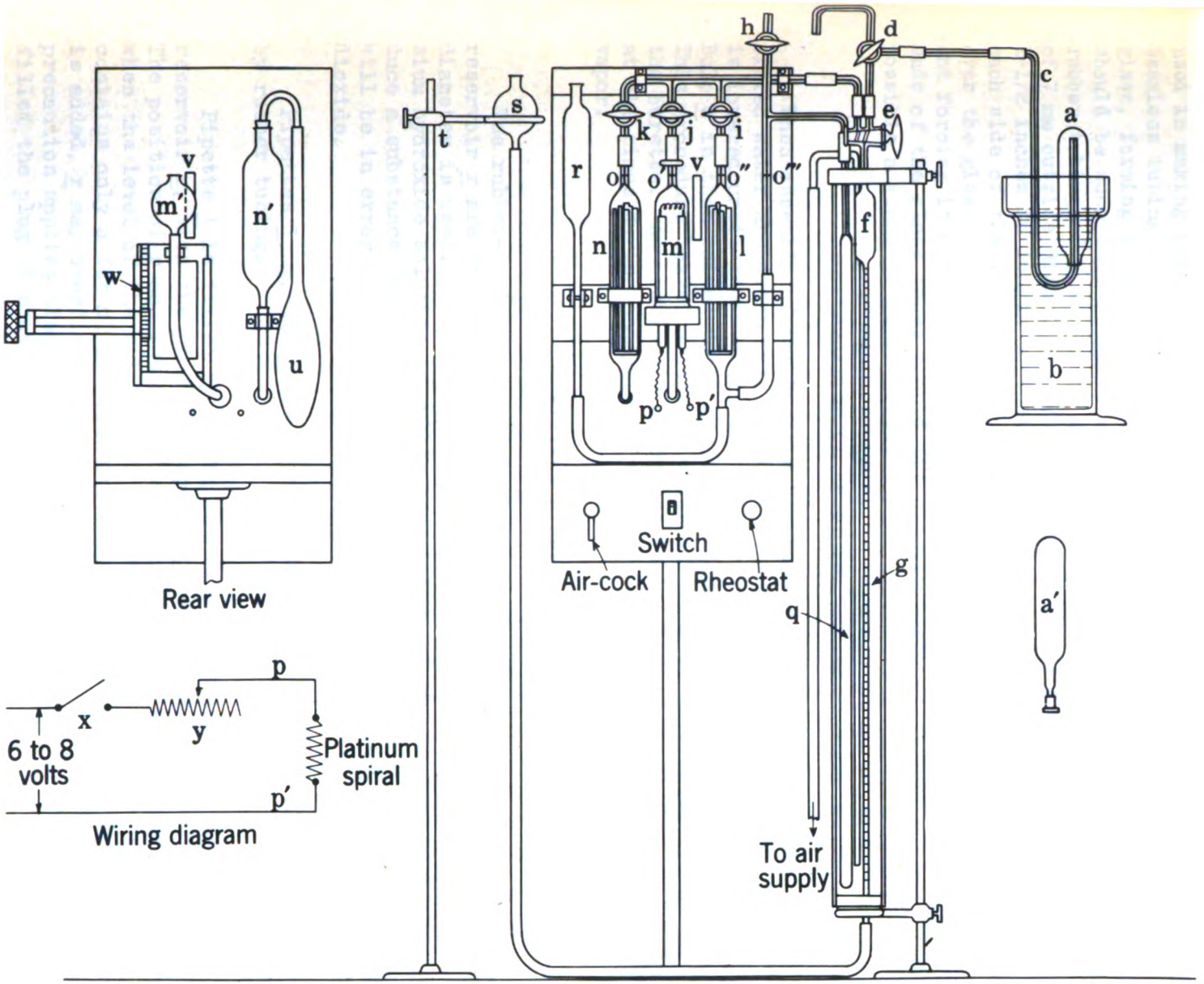

Figure 1.- Diagrammatic sketch of Bureau of Mines Haldane gas analysis apparatus.

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Making Rubber-Tubing Connections

It is important that rubber tubing of the proper type and size be used in making connections between the various parts of the apparatus. Seamless tubing of the "pure-gum" type is satisfactory, as it adheres to glass, forming a gastight joint. The inside diameter of the tubing should be such that it makes a snug fit with the glass. For example, rubber tubing of 5 mm inside diameter should be used to join glass tubes of 7 mm outside diameter. Rubber-tubing connections should be 1-1/4 to 1-1/2 inches in length so that the rubber extends 5/8 to 3/4 inch on each side of the junction of the glass tubes. Fitting the rubber tubing over the glass is facilitated by moistening the interior of the rubber and forcing it onto the glass with a reciprocating rotary motion. The ends of the glass tubes should fit closely together to make as nearly as possible a glass-to-glass joint.

Addition of Water to Burette

When assembly of the burette has been completed, 2 or 3 ml of distilled water are drawn into the burette through d, and leveling bulb s is lowered until the mercury in the burette reaches the 21 ml mark. Bulb s is then raised until mercury is discharged from the outlet of d. This procedure leaves a film of water adhering to the inside surface of the burette. As previously discussed, this film of water must be present at all times during analysis to saturate the gas in the burette with water vapor.

Filling Pipettes

The rubber-tubing connections between pipette l, tube o''', and reservoir r are installed next. Sulphur-free tubing of 6 to 8 mm inside diameter is used. Sulphur-free rubber is used, as the action of potassium hydroxide solution on rubber containing sulphur in time will produce a substance that absorbs oxygen, and carbon dioxide determinations will be in error owing to the absorption of oxygen in addition to carbon dioxide.

Pipettes l, m, and n are connected next to stopcocks i, j, and k by rubber tubing.

Pipette l is filled by adding potassium hydroxide solution to reservoir r, with the plug of stopcock i removed and stopcock h open. The position of r and the amount of solution added are so regulated that when the level of the solution in l rises to point o'' the bulb of r contains only a few ml of solution. If an excessive amount of solution is added, r may overflow when gas is introduced into pipette l. This precaution applies also to filling reservoirs n' and m'. When l is filled the plug of stopcock i is replaced.

Pipette n is filled by adding potassium pyrogallate to reservoir n', with the plug of stopcock k removed, until the solution rises to point o. The plug of stopcock k is replaced and rubber bag u is partly inflated and inserted in the opening of n' as shown.

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Combustion pipette m is filled by adding clean (preferably distilled) mercury to reservoir m', with plug of stopcock j removed, until the mercury rises to point o'. The plug of stopcock j is replaced when m is filled. The glass tubes that support the platinum spiral must be filled completely with mercury. This may be accomplished by adjusting the position of m' so the mercury level in m is just at the tops of the glass tubes and then tapping the pipette so small globules of mercury drop into the tubes until they are filled. An alternate procedure is to remove the rubber stopper (before mercury is added to the pipette) that supports the tubes and to fill them with mercury through a funnel with a small-diameter stem. When the stopper is reinserted in the pipette it should be moistened and pressed firmly into place to insure a gastight fit.

Adjusting Temperature of Platinum Spiral

When m has been filled the electric connections are attached, the mercury level is lowered until the spiral is exposed, and switch x is closed. The temperature of the spiral is adjusted by rheostat y so that the wire is at a bright yellow heat. It is important to heat the spiral enough to cause complete burning of combustible gases, but not to the extent of fusing the wire. Switch x is opened after the temperature of the spiral has been adjusted properly.

Greasing Stopcocks

All stopcocks are cleaned and greased. Greasing the stopcocks properly is an important part of the analytical procedure. Improper greasing is likely to cause errors in analysis and difficulties in manipulation of the apparatus.

A lubricant containing rubber, paraffin, and vaseline is used; preparation of a grease of this composition is described under Comments On Use and Care of Apparatus. The plug and barrel of the stopcock are cleansed by wiping with cheesecloth. The barrel may be cleaned by wrapping two or three layers of cheesecloth over the end of a lead pencil and passing this through the barrel with a rotary motion. The capillary openings may be cleaned by a pipe cleaner or soft copper wire. Instruments that might scratch the ground surfaces of the stopcock should not be used. The stopcock is lubricated by placing a thin layer of grease, extending the length of the plug, along the sides of the plug not pierced by the bore. The plug is inserted in the barrel, pressed firmly into place, and rotated several times in both directions. If greased properly, an even, transparent film of grease covers the ground surfaces of the stopcock at all points of contact. The proper amount of grease to apply is learned best by experience. If too little grease is applied, striations and bubbles will be evident, and the stopcock may leak. If an excess of grease is used the bore will become plugged in a short time, impeding or stopping flow of gas through the stopcock. Stopcock plugs usually are not interchangeable, and it is best to remove only one plug at a time to avoid confusion.

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Adjusting Levels of Liquids in Pipettes

The solutions in pipettes l and n and the mercury in pipette m are brought to o, o', and o''. by drawing about 20 ml of air into the burette and turning stopcock e to communicate with the manifold. Stopcock i is opened, and the level of the solution is adjusted to mark o'' by raising or lowering leveling-bulb s as necessary. This procedure, from the opening of stopcock i, must be conducted with care, as the caustic solution in l may easily be drawn into the manifold and possibly the burette. If this should occur all parts accidentally brought into contact with caustic solution must be cleaned thoroughly with dilute sulphuric acid.

The same procedure is used in bringing the liquids in pipettes n and m to marks o and o'. The precautions regarding manipulation of the caustic solution apply in adjusting the potassium pyrogallate solution in n to mark o.

Testing for Leaks

The apparatus is next tested for leaks. Stopcocks e and d are turned to communicate with the atmosphere, and leveling-bulb s is lowered until about 20 ml of air has been drawn into the burette. Stopcock e is then closed, and s is raised to the top of its supporting rod. A gradual rise in the level of mercury in the burette indicates a leak at stopcock e. If the mercury level remains stationary, turn e to communicate with the manifold. A gradual rise in mercury level in the burette indicates leakage at stopcocks i, j, or k or at the rubber-tubing connections between e and the manifold. Leakage at i, j, or k usually, but not always, causes the solutions to drop from marks o, o', and o''. If no leaks are indicated, the rubber-tubing connections below i, j, and k are tested next. Reservoirs n' and m' are lowered as far as possible and maintained in that position for several minutes. If no leaks are present in the rubber-tubing connections below stopcocks k and j, the liquids in pipettes n and m will return to marks o and o' when n' and m' are returned to their former positions. With stopcock h open, reservoir r is adjusted so that the solution in the compensator tube coincides with mark o'''. (If the level of the solution in l does not coincide with o'', it should be brought to that mark by opening i, adjusting leveling-bulb s and closing i.) Stopcock h is closed and r lowered as far as possible for several minutes. If a leak exists in the rubber connection below stopcock i, the solution will fail to return to o'' when r is returned to its former position; if the solution fails to return to mark o''', a leak exists in h or in the rubber connection with closed tube q.

Leaks at stopcocks may be corrected by regreasing or, if this fails, by regrinding (seeComments on Use and Care of Apparatus) and regreasing. Leaks at rubber-tubing connections may be corrected by replacing the tubing; if the tubing that leaked did not appear to fit tightly to the glass, it should be replaced by tubing of smaller inside diameter, or the joint between glass and rubber may be improved by wrapping the rubber connection, at about one-quarter inch from each end, with two strands of No. 22 copper wire, twisting the free ends of the wire together after wrapping.

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Stopcock d and rubber connections to U-tube c are tested for leaks by turning d to communicate with c, raising leveling-bulb s until the mercury in burette f rises to stopcock e, closing the outlet of c by placing a finger over the open end of the tube and lowering s. If the mercury level in f continues to fall, a leak is indicated between e and c.

ANALYTICAL PROCEDURE

Filling Manifold with Nitrogen

After the apparatus has been assembled and tested for leaks the first step in the analytical procedure is to fill the manifold from stopcock e to marks o, o', and o'' with nitrogen. As the manifold is not purged by the mercury in the burette when a sample is drawn into the apparatus, its volume is "dead space" and must be filled with a gas that is inert with respect to the various treatments to which the gas sample is subjected. To fill the manifold with nitrogen, 20 ml of air is drawn into the burette through stopcocks e and d; e is turned to communicate with the manifold, stopcock k is opened, and the air sample in burette f is passed back and forth between f and pipette n by raising and lowering leveling bulb s. Ten to twelve passes are usually sufficient to effect absorption of the oxygen from the air sample. (As an aid in determining when the oxygen has been absorbed, the color of the potassium pyrogallate solution adhering to the tubes in the pipette may be observed. While oxygen is being absorbed the film of reagent on these tubes becomes brownish-red. When the oxygen has been absorbed the reagent assumes a greenish hue. Four or five additional passes should be made after the red color no longer can be observed.) After the oxygen has been absorbed, the residual nitrogen[7] is withdrawn from n to burette f, and k is closed. The gas is then passed once into pipettes m and l to "pick up" the oxygen present in the capillaries below stopcocks i and j. When the gas is withdrawn from these pipettes the liquids in the pipettes are adjusted to marks o' and o'', and i and j are closed. The gas is again passed six times into n to remove the oxygen picked up in the capillaries below i and j. When this has been done the gas is returned to f, the liquid in n is brought to mark o, and k is closed.

Stopcocks i and h are opened and the level of the potassium hydroxide solution adjusted to marks o'' and o'''. Stopcocks i and h are then closed, and stopcock e is rotated 180°. This procedure leaves the manifold filled with nitrogen at "compensated pressure" and brings the air in the closed tube of the compensator to atmospheric pressure. Stopcock h must not be opened during an analysis, but may be opened between analyses to reestablish atmospheric pressure in the closed tube of the compensator and should be left open when the apparatus is not in use.

7/ As the potassium pyrogallate solution is alkaline, the carbon dioxide of the air is removed along with the oxygen. The residual nitrogen of the air contains about 1 percent of the "noble gases" (argon, neon, xenon, krypton, and helium), which are inert and which, in ordinary gas analysis, are included in the term "nitrogen".

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Drawing Sample into Burette

Stopcocks e and d are turned to communicate with U-tube c, and leveling bulb s is raised until mercury flows from the outlet of c. Stopcock e is then turned 90°.

If the gas to be analyzed is contained in a vacuum-type sample bottle, as shown in figure 1, a file mark is made on the neck of the bottle, the neck is placed under mercury in jar b and broken off by tapping against the side of the jar. The open end of the sample bottle is held beneath the mercury, and c is inserted as shown in figure 1. If the sample is contained in a tube having stopcocks at both ends, c is replaced by a short elbow of capillary tubing. One stopcock of the sample tube is attached to the outlet of this elbow and the other submerged in the mercury in jar b before opening.

After the sample tube has been connected s is lowered, e is turned to communicate with the sample, and 18 to 20 ml of sample is drawn into burette f. Stopcock d is then turned to communicate with the atmosphere, and s is raised until mercury flows from the outlet of d to prevent contamination of the sample by bubbles of air that may have been trapped in the capillary between U-tube c and stopcock e. Stopcock d is turned to communicate with the sample, and s is lowered until approximately 20 ml of sample has been drawn into f. The position of the sample tube is so adjusted that the levels of the mercury inside and outside the sample tube coincide, and e is turned to communicate with the manifold.

Reading Burette

Stopcock i is opened cautiously (the level of the solution in pipette l should not move very far in either direction from mark o'') and the positions of leveling-bulb s and reservoir r so adjusted that the solution in l is at mark o'' and that in the compensator tube at mark o'''. The volume of gas sample in burette f is then read to the nearest 0.002 ml, which gives the volume of sample taken for analysis.

The "compensating" procedure described in the foregoing paragraph - that is, the adjustment of the level of the potassium hydroxide solution to marks o'' and o''' - is followed throughout the analysis before each volume reading in the burette is made.

Determination of Carbon Dioxide

Carbon dioxide is removed from the sample by raising and lowering leveling-bulb s with stopcock i open, causing the gas to pass back and forth between burette f and pipette l. After six passes into l the gas is withdrawn to f, the level of the potassium hydroxide solution adjusted to marks o'' and o''' as previously described, and the burette reading taken. It is well to check this reading, until technique is perfected, by passing the gas into l six times more and again reading the burette. After the burette is read, stopcock i is closed. The burette reading is subtracted from the original volume of sample to obtain the volume of

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carbon dioxide in the sample. The percentage of carbon dioxide in the sample is calculated as follows:

$$\text{Percent, by volume, 8/ of carbon dioxide} = \frac{\text{volume of carbon dioxide}}{\text{original volume of sample}} \times 100.$$

Determination of Combustible Gases

Combustible gases are determined by opening stopcock j and passing the gas into pipette m, lowering reservoir m' at the same time so that the mercury levels in m and m' coincide. When the platinum spiral is exposed, switch x is closed. (The Haldane apparatus is not designed for the determination of combustible gas-air mixtures within the inflammable range. If an attempt is made to burn an inflammable mixture(see Appendix) in pipette m, an explosion may result. If there is doubt as to the amount of combustible in the sample, a piece of wire screen or shatterproof glass should be placed in front of the pipette to protect the operator.) To cool the pipette a stream of air is directed over it by a curved glass or metal tube (shown surrounding the capillary outlet of m in fig. 1) pierced on the lower side by a number of small holes. If the temperature of the platinum spiral has not been adjusted previously it should now be adjusted to the proper temperature. (See Preparation of Apparatus for Use.) The gas is passed back and forth between burette f and pipette m 8 to 10 times, keeping the mercury in m and m' at the same level. Switch x is opened and the pipette allowed to cool to room temperature. The gas is withdrawn to f, the mercury in m brought to mark o' and stopcock j closed. Stopcock i is opened, the level of the potassium hydroxide solution brought to marks o'' and o''', and the burette reading taken. This reading subtracted from that obtained after removal of the carbon dioxide gives the contraction in volume due to combustion.

Carbon dioxide produced by combustion is determined by passing the gas six times into l, compensating, and reading the burette. If the contraction due to combustion exceeds 0.200 ml, the sample should be subjected to combustion a second time and the carbon dioxide produced by the second combustion determined. The two contractions and the two carbon dioxide values are added to obtain the total contraction in volume and the total carbon dioxide produced by combustion. If methane is the only combustible gas in the sample, the percentage of methane is calculated from these values as follows:

$$\text{Volume of methane in sample} = \frac{\text{contraction caused by combustion} + \text{carbon dioxide formed}}{3}.$$

$$\text{Percent, by volume, of methane} = \frac{\text{volume of methane}}{\text{original volume of sample}} \times 100.$$

8/ The results of gas-volumetric analysis are reported as percent by volume, rather than percent by weight. The results usually are reported on a "dry basis", that is, no account is taken of the water-vapor content of the sample.

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Methods for calculating the volumes of combustible gases other than methane and of various combinations of combustible gases are given in the section on Calculation of Results.

Determination of Oxygen

Oxygen is removed from the sample by passing the gas into the potassium pyrogallate solution in pipette n. The gas is passed 12 times (this number of passes usually suffices but it is advisable to observe the color change in the solution, as previously mentioned) into pipette n and then is withdrawn to burette f, stopcock k is closed, and the gas is passed once into pipettes m and l to pick up oxygen remaining in the capillaries below stopcocks j and i. The gas is then passed six times more into n and withdrawn to f, the level of the solution in n being adjusted to mark o before k is closed. The volume of gas in the burette is compensated and the burette reading taken. It is well to check this reading by passing the gas again into n four or five times and taking a second burette reading. This reading, subtracted from the reading obtained after the final removal of carbon dioxide produced by combustion, gives the volume of oxygen remaining in the sample after combustion. If the sample contains combustible gas, a definite volume of oxygen has been consumed in the combustion, and this volume of oxygen must be calculated and added to the volume of oxygen determined by absorption to obtain the total volume of oxygen in the sample.

If methane is the only combustible gas in the sample the calculation is as follows:

Volume of oxygen consumed in combustion = 2 x volume of methane

Total volume of oxygen in sample = volume of oxygen determined by absorption + volume of oxygen consumed in combustion.

$$\text{Percent, by volume, of oxygen} = \frac{\text{total volume of oxygen}}{\text{original volume of sample}} \times 100$$

Calculation of oxygen consumed in combustion of various gases is illustrated in the section on Calculation of Results.

Determination of Nitrogen

The percentage of nitrogen is obtained by subtracting the sum of the percentages of the other constituents from 100:

Percent, by volume, of nitrogen = 100 - (percent carbon dioxide + percent combustible gas + percent oxygen).

CALCULATION OF RESULTS

In the preceding section, Analytical Procedure, the volume of methane in the sample was calculated by adding the contraction in volume and the carbon dioxide produced by combustion and dividing this sum by three.

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This calculation is based on the volume relations expressed by the reaction

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$$

One volume[9] of methane requires 2 volumes of oxygen for complete combustion, and 1 volume of carbon dioxide and 2 volumes of water vapor are formed. As the water vapor condenses and occupies negligible space, the carbon dioxide is the only measurable product of combustion. Therefore, 3 volumes of gas are reduced to 1 volume by combustion. In other words, the contraction produced by combustion of 1 volume of methane is twice the volume of the methane, and the carbon dioxide produced is equal to the volume of the methane, as shown in the following equations:

$$\text{Contraction} = 2 \times CH_4,$$

$$\text{Carbon dioxide} = CH_4.$$

Combining and solving these equations,

$$\text{Methane} = \frac{\text{contraction} + CO_2}{3}.$$

Formula for calculation of the volume of any single combustible gas may be derived in the same manner. For example, from the reaction

$$2\ CO + O_2 = 2\ CO_2,$$

$$\text{Carbon monoxide}\ [10] = 2/3\ (\text{contraction} + CO_2),$$

and from the reaction

$$2\ H_2 + O_2 = 2\ H_2O,$$

$$\text{Hydrogen} = 2/3\ \text{contraction}.$$

These reactions indicate also that carbon monoxide and hydrogen require one-half their volume of oxygen for complete combustion.

9/ The term "volume" means any unit volume, as milliliter, cubic inch, cubic foot, etc.

10/ If a sample is suspected of containing carbon monoxide in amounts at, or near, the limit of accuracy of the Haldane apparatus, the gas-volumetric analysis should be supplemented by tests specific for carbon monoxide, as the pyrotannic acid method, to verify the presence or absence of this gas. See Sayers, R. R., and Yant, W. P., The Pyrotannic Acid Method for the Quantitative Determination of Carbon Monoxide in Blood and in Air: Tech. Paper 373, Bureau of Mines, 1925, 18 pp.

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

BUREAU OF MINES HALDANE GAS-ANALYSIS APPARATUS

By L. B. Berger and H. H. Schrenk

ERRATA

Page 16, line 2: "$CH_4 + 2\ O_2 + 2\ H_2O$ " should read

"$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$."

Page 20, line 16: The value "49.69" should be "79.69."

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The following example illustrates data relating to analysis of a sample of coal-mine air containing carbon dioxide, methane, oxygen, and nitrogen:

Analytical Data

	Burette reading, ml	Difference, ml
Volume of sample taken for analysis	20.010	
Volume after carbon dioxide absorption	19.978	
Contraction due to carbon dioxide absorption		0.032
Volume after combustion	19.922	
Contraction due to combustion		.056
Volume after carbon dioxide absorption	19.894	
Carbon dioxide due to combustion		.028
Volume after absorption of residual oxygen	15.820	
Residual oxygen		4.074
Osygen consumed in combustion of methane		.056
Total oxygen		4.130

Calculation of Results

		Percent by volume
Carbon dioxide	$\frac{0.032}{20.010} \times 100$	0.16
Methane	$\frac{0.056 + 0.028}{3} = 0.028$	
	$\frac{0.028}{20.010} \times 100$	.14
Oxygen	$(2 \times 0.028) + 4.074 = 4.130$	
	$\frac{4.130}{20.010} \times 100$	20.64
Nitrogen (by difference)	$100 - (0.16 + 0.14 + 20.64)$	79.06

The volume of each gas in mixtures containing any two of the gases methane, carbon monoxide, and hydrogen may be calculated from contraction and carbon dioxide produced by combustion. The calculations are based on the following reactions:

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O, \quad (1)$$

$$2\ CO + O_2 = 2\ CO_2, \quad (2)$$

$$2\ H_2 + O_2 = 2\ H_2O. \quad (3)$$

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Methane and carbon monoxide. - When methane and carbon monoxide are present the following relations are obtained from equations (1) and (2):

$$\text{Contraction} = 2 \times CH_4 + 1/2\ CO, \quad (4)$$

$$\text{Carbon dioxide} = CH_4 + CO. \quad (5)$$

Solving equations (4) and (5),

$$\text{Methane} = \frac{2 \times \text{contraction} - CO_2}{3},$$

$$\text{Carbon monoxide} = CO_2 - CH_4.$$

Methane and hydrogen. - When methane and hydrogen are present the following relations are obtained in like manner from equations (1) and (3):

$$\text{Methane} = CO_2,$$

$$\text{Hydrogen} = \frac{2 \times \text{contraction} - 4 \times CO_2}{3}.$$

Hydrogen and carbon monoxide. - When hydrogen and carbon monoxide are present the following relations are obtained from equations (2) and (3):

$$\text{Hydrogen} = \frac{2 \times \text{contraction} - CO_2}{3},$$

$$\text{Carbon monoxide} = CO_2.$$

Methane, carbon monoxide and hydrogen. - When methane carbon monoxide, and hydrogen are present, the volume of oxygen consumed by combustion must be determined in addition to the contraction and carbon dioxide produced by combustion to calculate the volume of each gas. The volume of oxygen consumed is determined by subjecting one portion of the sample to the complete procedure - determination of carbon dioxide, contraction due to combustion, carbon dioxide produced by combustion and residual oxygen remaining after combustion - and analyzing a second portion of the sample for carbon dioxide and oxygen only. The oxygen consumed by combustion in the first portion is calculated as follows:

First portion (A) - carbon dioxide, contraction and carbon dioxide produced by combustion and residual oxygen determined.

Second portion (B) - carbon dioxide and oxygen determined.

$$\text{Percent oxygen in B} = \frac{\text{volume of oxygen determined}}{\text{original volume of sample}} \times 100.$$

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$$\text{Total volume oxygen in A} = \frac{\text{original volume of A x percent oxygen in B}}{100}.$$

Volume oxygen consumed in combustion of A = total volume oxygen in A - volume residual oxygen in A.

From equations (1), (2), and (3) the following relations are obtained:

$$\text{Hydrogen} = \text{contraction} - \text{oxygen consumed},$$

$$\text{Methane} = \frac{(2 \times \text{contraction} - CO_2)}{3} - H_2$$

$$\text{Carbon monoxide} = CO_2 - CH_4.$$

When two or more gases are determined by combustion the small, unavoidable errors of analysis may be multiplied in the calculations, thus reducing to some extent the accuracy and precision of determination of these gases.

A typical analysis of a sample containing carbon dioxide, hydrogen, methane, carbon monoxide, oxygen, and nitrogen follows:

First Portion

	Burette reading, ml	Difference, ml
Volume of sample taken for analysis	20.430	
Volume after carbon dioxide absorption	20.185	
Contraction due to carbon dioxide absorption		0.245
Volume after combustion	20.118	
Contraction due to combustion		.067
Volume after carbon dioxide absorption	20.070	
Carbon dioxide due to combustion		.048
Volume after oxygen absorption	16.280	
Residual oxygen		3.790

Second Portion

Volume of sample taken for analysis	20.270	
Volume after carbon dioxide absorption	20.024	
Contraction due to carbon dioxide		.246
Volume after oxygen absorption	16.204	
Contraction due to oxygen absorption		3.820

Calculations

From analysis of the second portion the oxygen content of the sample is $\frac{3.820}{20.270} \times 100$, or 18.85 percent by volume.

Total volume of oxygen in first portion =

$$\frac{20.430 \times 18.85}{100} = 3.851 \text{ ml.}$$

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Volume oxygen consumed in combustion of first portion = 3.851 - 3.790 (residual oxygen of first portion) = 0.061 ml.

Volume hydrogen in first portion = contraction - oxygen consumed =

$$0.067 - 0.061 = 0.006 \text{ ml.}$$

Volume methane in first portion = $\frac{2 \times \text{contraction} - CO_2}{3} - H_2 =$

$$\frac{0.134 - 0.048}{3} - 0.006 = 0.023 \text{ ml.}$$

Volume carbon monoxide in first portion = $CO_2 - CH_4 = 0.048 - 0.023 = 0.025$ ml.

Results of Analysis

	Percent by volume
Oxygen = $\frac{3.820}{20.270} \times 100$ (from analysis of second portion) =	18.85
Carbon dioxide = $\frac{0.245}{20.430} \times 100$ (from analysis first portion) =	1.20
Hydrogen = $\frac{0.006}{20.430} \times 100$ (from analysis first portion) =	.03
Methane = $\frac{0.023}{20.430} \times 100$ (from analysis first portion) =	.11
Carbon monoxide = $\frac{0.025}{20.430} \times 100$ (from analysis first portion) =	.12
Nitrogen (by difference) = 100 - (18.85 + 1.20 + 0.03 + 0.11 + 0.12) =	~~49.69~~ 79.69

Hydrocarbon-air mixtures. - Saturated hydrocarbons of the formula $C_nH_{2n} + 2$, such as natural gas and gasoline vapor, may be calculated from the following equation:

$$\text{Volume of hydrocarbons} = \frac{2 \times \text{contraction} - CO_2.}{3}$$

If the combustible consists mainly of higher hydrocarbons, as "wet" natural gas or gasoline vapor, it is advisable to determine only contraction and carbon dioxide produced by combustion, as these higher hydrocarbons are appreciably soluble in the potassium hydroxide solution, and if the sample is passed first into this solution to determine carbon dioxide error may be introduced through solubility. If the sample consists of hydrocarbons and normal air, correction may be applied to the combustion data for the carbon dioxide content of the air (0.03 percent).

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COMMENTS ON USE AND CARE OF APPARATUS

Location of Apparatus

The Haldane apparatus should be installed in a location free from drafts and not subject to wide variations or sudden changes in temperature. Sudden changes in temperature during an analysis may cause the level of the liquid in the compensating tube to move beyond the working range of the apparatus.

Calibration of Burette

The burette is calibrated while in the water jacket, which is filled with water and maintained at as nearly constant temperature as possible. A thermometer inserted in the water jacket indicates the temperature. A two-way stopcock is sealed to the lower end of the burette, mercury is introduced into the burette through a leveling-bulb and rubber tubing attached to one outlet of this stopcock, and mercury is added until it reaches the bottom of the stopcock at the upper end of the burette. Successive portions of mercury are withdrawn through the open outlet of the lower stopcock and weighed. The burette reading is noted after each portion is withdrawn. The true volume of each portion is calculated from its weight and observed temperature.

Precautions Against Contamination of Apparatus by Caustic Solutions

It is of utmost importance to keep the stopcocks, manifold, combustion pipette, and burette free of the slightest traces of potassium hydroxide or potassium pyrogallate solutions if accurate analyses are to be obtained. Even though the solutions have not been observed to enter these parts of the apparatus, it is advisable to cleanse them if the results of analysis seem doubtful and no other cause of error is evident. The mercury used in displacing the sample from its container and all connections to the sample container also must be kept free of caustic.

Cleaning Manifold

The best method of cleaning the manifold is to remove it from the apparatus and draw through it, in the order named, dilute sulphuric acid, distilled water, and air.

Cleaning Burette

The burette may be cleaned by a mixture of equal parts of concentrated sulphuric acid and saturated potassium dichromate solution. An alternate procedure is to draw into the burette a solution of 90 percent concentrated nitric acid and 10 percent water, allow it to remain for a few minutes, and then discharge it. A solution containing 50 percent concentrated nitric acid is used next, followed by solutions containing 25 and 5 percent concentrated nitric acid, and finally the burette is washed several times with distilled water. This may be done without draining the mercury from the system, as the gradual decrease in acid concentration prevents deposition of mercurous nitrate on the walls of the burette.

Note: Organic solvents should not be used to clean any part of the apparatus.

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Preparation of Stopcock Grease

Stopcock grease of the following composition is suitable for use with the Haldane apparatus:

Smoked sheet or pale crepe rubber - 10 parts, by weight.
Vaseline - 18 parts, by weight.
Paraffin - 1 part, by weight.

The rubber is cut into small pieces, mixed with the other ingredients, and heated gently until the rubber goes into solution. The grease is then heated to 155° C. for 100 to 200 hours. The composition of the grease may be varied to suit the needs of the user by changing the relative proportions of the constituents; if the grease appears too viscous, the proportion of vaseline may be increased, or if too fibrous or stringy, the proportion of rubber may be decreased.

Grinding Stopcocks

If stopcocks are unsatisfactory due to poor fit between plug and barrel, or if they become eroded by wear or the action of caustic solutions they may be reground by the following procedure: The plug of the stopcock is given a thin coating of moistened abrasive (400- to 600-mesh), inserted in the barrel lightly, and turned with a reciprocating rotary motion. The plug is withdrawn from the barrel after each four or five turns to prevent formation of grooves in the ground surfaces. At intervals the stopcock is washed free of abrasive, dried, and greased. When an even, transparent film of grease is obtained between plug and barrel at all points of contact, grinding is complete. (If the stopcock is deeply eroded so much grinding may be necessary that the capillary bores are thrown out of alinement and the stopcock becomes useless.)

Analysis of Normal Air to Check Analytical Procedure

Technique of operation and condition of apparatus may be considered satisfactory when the results obtained in analysis of normal air agree, within the limits of accuracy of the apparatus, with its actual composition (0.03 percent carbon dioxide, 20.93 percent oxygen, 0.00 percent combustible, and 79.04 percent nitrogen).

Difficulties Encountered in Use of Haldane Apparatus

In the use of the Haldane apparatus, as with any analytical procedure, difficulties may be encountered, and their sources are determined most readily by systematic consideration of their possible causes. The difficulties most commonly encountered in the use of the Haldane apparatus, and their possible causes, are:

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Difficulty encountered	Possible causes
Leaks in apparatus:	Defective or deteriorated rubber tubing; tubing of improper size; improperly greased or poorly fitting stopcocks; defects in glassware; rubber stopper at base of combustion pipette improperly fitted; faulty glass-platinum seal in combustion pipette electrodes.
Expansion in volume when carbon dioxide is determined:	Leaks; insufficient water in burette to maintain sample in saturated condition.
Incorrect value for oxygen percentage in analysis of normal air:	Leaks; insufficient water in burette; potassium pyrogallate solution exhausted; absorption of nitrogen by fresh potassium pyrogallate solution; oxygen not completely absorbed; burette dirty or improperly calibrated.
Repeat burette readings do not agree in determination of a particular constituent:	Leaks; solutions exhausted; constituent not completely absorbed; in determination of combustibles, temperature of platinum spiral may be too low.
Expansion in volume after combustion:	Leaks; sample does not contain enough oxygen for complete combustion of combustibles.
Faulty combustion data: For example, methane is known to be the only combustible gas present, but ratio of contraction to carbon dioxide produced is not 2 to 1.	Leaks; insufficient water in burette; potassium hydroxide or potassium pyrogallate solution present in manifold, burette, or combustion pipette.
Liquid in compensating device appears sluggish in movement:	Capillary between burette and potassium hydroxide pipette blocked by globule of water, mercury, or stopcock grease.
Liquids do not remain at marks in capillaries of pipettes:	Leaks; manifold not filled with inert gas.
Duplicate analyses do not agree within satisfactory limits:	Any of the foregoing causes.

SUMMARY

The Haldane-type gas-analysis apparatus used by the Bureau of Mines is described in this publication with regard to its application, accuracy precision, limitations, construction, and operation. Methods of calculating results of analysis of various gas mixtures, comments on use and care of the apparatus, and discussion of causes of the most commonly occurring difficulties encountered in use of the apparatus are included.

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APPENDIX

Properties of some combustible gases and vapors

Gas or vapor	Formula	Molecular weight	Specific gravity (air = 1)	Limits of inflammability 1/ in air, percent by volume	
				Lower limit	Upper limit
Methane	CH_4	16.041	0.5545 2/	5.0	15.0
Ethane	C_2H_6	30.067	1.0493 2/	3.1	12.5
Propane	C_3H_8	44.092	1.5625 2/	2.4	9.5
Butane	C_4H_{10}	58.118	2.0100 2/	1.9	8.5
Pentane	C_5H_{12}	72.144	2.4921 3/	1.4	7.8
Gasoline				1.3	7.0 4/
Ethylene	C_2H_4	28.051	.9748 2/	2.7	28.6
Propylene	C_3H_6	42.077	1.4535 3/	2.0	11.1
Butylene	C_4H_8	56.102	1.9380 3/	1.7	9.0
Pentylene	C_5H_{10}	70.128	2.4225 3/	1.6	--
Acetylene	C_2H_2	26.036	.9121 2/	2.5	80.5/
Benzene	C_6H_6	78.107	2.6981 3/	1.4	6.8
Carbon Monoxide	CO	28.010	.9672 2/	12.5	74.2
Hydrogen	H_2	2.0156	.0695 2/	4.0	74.2

1/ The lower and upper limits of inflammability are, respectively, the minimum and maximum amounts of combustible gas which, when mixed with air or other supporter of combustion, render the mixture inflammable. The values shown are those acdepted as most reliable by the Bureau of Mines at the time of preparation of this publication. The limits shown represent mixtures with normal air at ordinary temperatures and pressures. In general, mixing combustible gases with oxygen rather than air, has little effect on the lower limit, but raises the upper limit.

2/ Observed value: From data assembled by Bureau of Mines.

3/ Calculated as perfect gas: Although gases of this nature may deviate from the gas laws in the pure state, they will behave, for practical purposes, as perfect gases when present in the low concentrations that may be determined in the Haldane apparatus.

4/ The composition of gasoline is variable; the limits of inflammability will vary with composition.

5/ Upper limits of acetylene-air mixtures vary widely with experimental conditions; under some conditions propagation of flame has been observed in mixtures containing 80 percent acetylene.

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